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**EUROPEAN PATENT APPLICATION**

21 Application number: 89311572.5

22 Date of filing: 08.11.89

51 Int. Cl.<sup>5</sup>: **C10M 143/02, C10M 145/10, C10M 149/06, C10M 159/12, C08F 255/02, //(C10M143/02, 143:00),(C10M145/10,143:02, 143:00),(C10M149/06,143:02, 143:00),(C10M159/12,129:08, 129:93,133:04,133:08,133:38, 143:02),(C08F255/02,222:06), C10N20:02,C10N30:02, C10N30:04**

30 Priority: 14.11.88 US 270697

43 Date of publication of application: 23.05.90 Bulletin 90/21

84 Designated Contracting States: BE DE ES FR GB IT NL

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54 Improved multifunctional viscosity Index Improver.

57 Oleaginous compositions, particularly lubricating oil compositions, exhibiting improved low temperature viscometric properties containing a viscosity index improving effective amount of a multifunctional viscosity index improver comprised of the reaction products of:

(a) an oil soluble ethylene copolymer comprising from about 15 to 90 wt. % ethylene and from about 10 to 85 wt. % of at least one C<sub>3</sub> to C<sub>28</sub> alpha-olefin, having a number average molecular weight of from about 5,000 to 500,000, grafted with an ethylenically unsaturated carboxylic acid material having 1 or 2 acid or anhydride moieties;

(b) an organic polyamine having at least two reactive amine groups selected from primary and secondary amine groups, or a polyol; and

(c) poly-n-butene substituted dicarboxylic acid material, wherein said poly-n-butene has a number average molecular weight of from about 300 to about 3,000.

EP 0 369 674 A1

## IMPROVED MULTIFUNCTIONAL VISCOSITY INDEX IMPROVER

BACKGROUND OF THE INVENTION

The concept of derivatizing viscosity index (V.I.) improving high molecular weight ethylene copolymers with acid moieties such as maleic anhydride, followed by reaction with an amine to form a multifunctional viscosity index improver oil additive is known in the art and is described in the patent literature. This concept is described, for example, in the following patents:

U.S. Pat. No. 3,316,177 teaches ethylene copolymers such as ethylene-propylene, or ethylene-propylene-diene, which are heated to elevated temperatures in the presence of oxygen so as to oxidize the polymer and cause its reaction with maleic anhydride which is present during the oxidation. The resulting polymer can then be reacted with alkylene polyamines.

U.S. Pat. No. 3,326,804 teaches reacting ethylene copolymers with oxygen or ozone, to form a hydroperoxidized polymer, which is grafted with maleic anhydride followed by reaction with polyalkylene polyamines.

U.S. Pat. No. 4,089,794 teaches grafting the ethylene copolymer with maleic anhydride using peroxide in a lubricating oil solution, wherein the grafting is preferably carried out under nitrogen, followed by reaction with polyamine.

U.S. Pat. No. 4,137,185 teaches reacting C<sub>1</sub> to C<sub>30</sub> mono carboxylic acid anhydrides, and dicarboxylic acid anhydrides, such as acetic anhydride, succinic anhydride, etc. with an ethylene copolymer reacted with maleic anhydride and a polyalkylene polyamine to inhibit cross linking and viscosity increase due to further reaction of any primary amine groups which were initially unreacted.

U.S. Pat. No. 4,144,181 is similar to 4,137,185 in that it teaches using a sulfonic acid to inactivate the remaining primary amine groups when a maleic anhydride grafted ethylene-propylene copolymer is reacted with a polyamine.

U.S. Pat. No. 4,169,063 reacts an ethylene copolymer in the absence of oxygen and chlorine at temperatures of 150 °C to 250 °C with maleic anhydride followed by reaction with polyamine.

A number of prior disclosures teach avoiding the use of polyamine having two primary amine groups to thereby reduce cross-linking problems which become more of a problem as the number of amine moieties added to the polymer molecule is increased in order to increase dispersancy.

German Published Application No. P3025274.5 teaches an ethylene copolymer reacted with maleic anhydride in oil using a long chain alkyl hetero or oxygen containing amine.

U.S. Pat. No. 4,132,661 grafts ethylene copolymer, using peroxide and/or air blowing, with maleic anhydride and then reacts with a primary-tertiary diamine.

U.S. Pat. No. 4,160,739 teaches an ethylene copolymer which is grafted, using a free radical technique, with alternating maleic anhydride and a second polymerizable monomer such as methacrylic acid, which materials are reacted with an amine having a single primary, or a single secondary, amine group.

U.S. Pat. No. 4,171,273 reacts an ethylene copolymer with maleic anhydride in the presence of a free radical initiator and then with mixtures of C<sub>4</sub> to C<sub>12</sub> n-alcohol and amine such as N-aminopropylmorpholine or dimethylamino propyl amine to form a V.I. dispersant pour depressant additive.

U.S. Pat. No. 4,219,432 teaches maleic anhydride grafted ethylene copolymer reacted with a mixture of an amine having only one primary group together with a second amine having two or more primary groups.

German published application No. 2753569.9 shows an ethylene copolymer reacted with maleic anhydride by a free radical technique and then reacted with an amine having a single primary group.

German published application No. 2845288 grafts maleic anhydride on an ethylene-propylene copolymer by thermal grafting at high temperatures and then reacts with amine having one primary group.

French published application No. 2423530 teaches the thermal reaction of an ethylene copolymer with maleic anhydride at 150 °C to 210 °C followed by reaction with an amine having one primary or secondary group.

The early patents such as U.S. Pat. Nos. 3,316,177 and 3,326,804 teach the general concept of grafting an ethylene-propylene copolymer with maleic anhydride and then reacting with a polyalkylene polyamine such as polyethylene amines. Subsequently, U.S. Pat. No. 4,089,794 was directed to using an oil solution for free radical peroxide grafting the ethylene copolymer with maleic anhydride and then reacting with the polyamine. This concept had the advantage that by using oil, the entire reaction could be carried out in an oil solution to form an oil concentrate, which is the commercial form in which such additives are sold. This was an advantage over using a volatile solvent for the reactions, which has to be subsequently removed and

replaced by oil to form a concentrate. Subsequently, in operating at high polyamine levels in order to further increase the dispersing effect, increased problems occurred with the unreacted amine groups cross-linking and thereby causing viscosity increase of the oil concentrate during storage and subsequent formation of haze and in some instances gelling. Even though one or more moles of the alkylene polyamine was used per mole of maleic anhydride during imide formation, cross-linking became more of a problem as the nitrogen content of the polymers was increased. One solution was to use the polyamines and then to react the remaining primary amino groups with an acid anhydride, preferably acetic anhydride, of U.S. Pat. No. 4,137,185 or the sulfonic acid of U.S. Pat. No. 4,144,181. The cross-linking problem could also be minimized by avoidance of the ethylene polyamines and instead using amines having one primary group which would react with the maleic anhydride while the other amino groups would be tertiary groups which were substantially unreactive. Patents or published applications showing the use of such primary tertiary amines noted above are U.S. Pat. No. 4,219,432, wherein a part of the polyamine was replaced with a primary tertiary amine; U.S. Pat. No. 4,132,661; U.S. Pat. No. 4,160,739; U.S. Pat. No. 4,171,273; German No. P2753569.9; German No. 2,845,288; and French No. 2,423,530.

Still another problem which arose when using free radical initiators with mineral oil as the grafting medium is that as the grafting levels were increased to increase the dispersancy level, a larger proportion of the oil molecules in turn became grafted with the maleic anhydride. Then upon subsequent reaction with the amine these grafted oil particles tended to become insoluble and to form haze. To avoid using initiators, such as peroxides, for grafting and to avoid the use of oil, several of the above-noted patents utilized thermal grafting in solvent, preferably while using an ethylene copolymer containing a diene monomer so as to achieve an "ene" type reaction between the unsaturation resulting from the diene moiety and the maleic anhydride. However, generally such "ene" reactions are slower and less efficient than peroxide grafting.

U.S. Patent No. 4,517,104 represents a further improvement over the art in that it permits the utilization of the generally less expensive polyalkylene polyamines having two reactive amine groups such as primary and/or secondary amine groups, while achieving good dispersancy levels, inhibiting cross-linking and allowing initiator, e.g. peroxide, grafting in oil. This can be obtained by reacting the polymer grafted with the maleic anhydride and an acid component, such as an alkenyl succinic anhydride, e.g., polyisobutenyl succinic anhydride, with the polyalkylene polyamine, e.g. polyethyleneamine, or by reacting the polymer grafted with maleic anhydride with the reaction product of the acid component and the polyalkylene polyamine. In either case cross-linking between ethylene copolymer molecules is reduced or inhibited since many of the polyamine molecules will have one reactive amino group reacted with a maleic anhydride moiety of the ethylene copolymer while its other reactive amine group reacts with the acid component. A further advantage is that when the grafting is carried out in an oil solution using a free radical initiator, e.g. a peroxide, which is generally much faster with better control than thermal cracking or degradation, oil molecules which become grafted with maleic anhydride and reacted with the amine will, to a substantial extent, be solubilized if a long chain acid component is used.

While the multifunctional viscosity index improvers and oil compositions containing these V.I.-dispersants disclosed in U.S. Patent No. 4,517,104 are generally quite useful and advantageous, there nevertheless exists a need for oil compositions containing V.I.-dispersants exhibiting improved, i.e., reduced, low temperature viscometric properties as measured, for example, in the cold cranking simulator (CCS), ASTM D2602, than exhibited by oil compositions containing these known multifunctional viscosity index improvers. The improved low temperature viscometric properties are intended to facilitate engine starting in cold weather and to ensure pumpability, i.e., the cold oil should readily flow or slump into the well for the oil pump, otherwise the engine can be damaged due to insufficient lubrication. The present invention provides such multifunctional viscosity index improvers and oil compositions containing same.

### SUMMARY OF THE INVENTION

The present invention is directed to multifunctional viscosity index improvers comprising the reaction products of (i) ethylene copolymers grafted with ethylenically unsaturated carboxylic acid moieties, (ii) polyamines or polyols, and (iii) poly-n-butene substituted dicarboxylic acid material containing a poly-n-butene of from about 300 to about 3,000 number average molecular weight. Oleaginous compositions containing these multifunctional viscosity index improvers, which function as dispersants and viscosity index improvers, exhibit improved low temperature viscometric properties.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention there are provided oil soluble viscosity index improver-dispersant additives comprising the reaction products of (i) ethylene copolymers, such as copolymers of ethylene and propylene, grafted with ethylenically unsaturated carboxylic acid moieties, preferably maleic anhydride moieties; (ii) polyamines having two or more reactive amine groups selected from primary and secondary amine groups, or polyols; and (iii) poly-n-butene substituted carboxylic acid material wherein the poly-n-butene has a number average molecular weight of from about 300 to about 3,000. The multifunctional viscosity index improvers of the instant invention containing the poly-n-butene substituted dicarboxylic acid material when incorporated into oleaginous compositions such as lubricating oil compositions, result in oil compositions exhibiting improved, i.e., decreased, low temperature viscosity characteristics relative to similar conventional multifunctional viscosity index improvers, e.g., V.I.-dispersants, wherein the hydrocarbyl substituted carboxylic acid material is a polyisobutenyl substituted carboxylic acid material. That is to say by utilizing the poly-n-butene substituted dicarboxylic acid material in place of the polyisobutene substituted dicarboxylic acid material, V.I.-dispersants exhibiting improved low temperature viscometric properties are provided.

ETHYLENE COPOLYMER

Oil soluble ethylene copolymers used in the invention generally will have a number average molecular weight ( $\overline{M}_n$ ) of from above about 5000 to about 500,000; preferably 10,000 to 200,000 and optimally from about 20,000 to 100,000. In general, polymers useful as V.I. improvers will be used. These V.I. improvers will generally have a narrow range of molecular weight, as determined by the ratio of weight-average molecular weight ( $\overline{M}_w$ ) to number-average molecular weight ( $\overline{M}_n$ ). Polymers having a  $\overline{M}_w/\overline{M}_n$  of less than 10, preferably less than 7, and more preferably 4 or less are most desirable. As used herein ( $\overline{M}_n$ ) and ( $\overline{M}_w$ ) are measured by the well known techniques of vapor phase osmometry (VPO), membrane osmometry and gel permeation chromatography. In general, polymers having a narrow range of molecular weight may be obtained by a choice of synthesis conditions such as choice of principal catalyst and cocatalyst combination, addition of hydrogen during the synthesis, etc. Post synthesis treatment such as extrusion at elevated temperature and under high shear through small orifices, mastication under elevated temperatures, thermal degradation, fractional precipitation from solution, etc. may also be used to obtain narrow ranges of desired molecular weights and to break down higher molecular weight polymer to different molecular weight grades for V.I. use.

These polymers are prepared from ethylene and ethylenically unsaturated hydrocarbons including cyclic, alicyclic and acyclic, containing from 3 to 28 carbons, e.g. 3 to 18 carbons. These ethylene copolymers may contain from 15 to 90 wt. % ethylene, preferably 30 to 80 wt. % of ethylene and 10 to 85 wt. %, preferably 20 to 70 wt. % of one or more  $C_3$  to  $C_{28}$ , preferably  $C_3$  to  $C_{18}$  more preferably  $C_3$  to  $C_8$ , alpha olefins. While not essential, such copolymers preferably have a degree of crystallinity of less than 25 wt. %, as determined by X-ray and differential scanning calorimetry. Copolymers of ethylene and propylene are most preferred. Other alpha-olefins suitable in place of propylene to form the copolymer, or to be used in combination with ethylene and propylene to form a terpolymer, tetrapolymer, etc., include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, etc.; also branched chain alpha-olefins, such as 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-pentene, and 6-methylheptene-1, etc., and mixtures thereof.

The term copolymer as used herein, unless otherwise indicated, includes terpolymers, tetrapolymers, etc., of ethylene, said  $C_3$ - $C_{28}$  alpha-olefin and/or a non-conjugated diolefin or mixtures of such diolefins which may also be used. The amount of the non-conjugated diolefin will generally range from about 0.5 to 20 mole percent, preferably about 1 to about 7 mole percent, based on the total amount of ethylene and alpha-olefin present.

Representative examples of non-conjugated dienes that may be used as the third monomer in the terpolymer include:

- a. Straight chain acyclic dienes such as: 1,4-hexadiene; 1,5-heptadiene; 1,6-octadiene.
- b. Branched chain acyclic dienes such as: 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 3,7-dimethyl-1,7-octadiene; and the mixed isomers of dihydro-myrcene and dihydro-cymene.
- c. Single ring alicyclic dienes such as: 1,4-cyclohexadiene; 1,5-cyclooctadiene; 1,5-cyclo-

dod cadien ; 4-vinylcyclohexen ; 1-allyl, 4-isopropylidene cyclohexane; 3-allyl-cyclopentene; 4-allyl cyclohexene and 1-isopropenyl-4-(4-butenyl) cyclohexane.

d. Multi-single ring alicyclic dienes such as: 4,4'-dicyclopentenyl and 4,4'-dicyclohexenyl dienes.

e. Multi-ring alicyclic fused and bridged ring dienes such as: tetrahydroindene; methyl tetrahydroindene; dicyclopentadiene; bicyclo (2.2.1)-hepta-2,5-diene; alkyl, alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as: ethyl norbornene; 5-methylene-6-methyl-2-norbornene; 5-methylene-6, 6-dimethyl-2-norbornene; 5-propenyl-2-norbornene; 5-(3-cyclopentenyl)-norbornene and 5-cyclohexylidene-2-norbornene; norbornadiene; etc.

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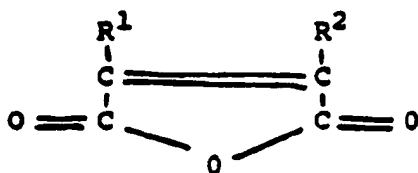
### ETHYLENICALLY UNSATURATED CARBOXYLIC ACID MATERIAL

These materials which are grafted onto the ethylene copolymer to make the acid grafted ethylene copolymer are (i) monounsaturated  $C_4$  to  $C_{10}$  dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, (i.e. located on adjacent carbon atoms) and (b) are at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; or with (ii) derivatives of (i) such as anhydrides or  $C_1$  to  $C_5$  alcohol derived mono-or diesters of (i). Upon reaction with the ethylene copolymer, the monounsaturations of the dicarboxylic acid, anhydride, or esters becomes saturated. Thus, for example, maleic anhydride becomes succinic anhydride.

Exemplary of such unsaturated mono and dicarboxylic acids, or anhydrides and esters thereof are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, etc.

Maleic anhydride or a derivative thereof is preferred as it does not appear to homopolymerize appreciably but grafts onto the ethylene copolymer to give two carboxylic acid functionalities. Such preferred materials have the generic formula

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wherein  $R^1$  and  $R^2$  are independently hydrogen or chlorine.

As taught by U.S. 4,160,739 and U.S. 4,161,452, both of which are incorporated herein by reference, various unsaturated comonomers may be grafted on the olefin copolymer together with the unsaturated acid component, e.g. maleic anhydride. Such graft monomer systems may comprise one or a mixture of comonomers different from the unsaturated acid component and which contain only one copolymerizable double bond and are copolymerizable with said unsaturated acid component. Typically, such comonomers do not contain free carboxylic acid groups and are esters containing alpha, beta-ethylenic unsaturation in the acid or alcohol portion; hydrocarbons, both aliphatic and aromatic, containing alpha, beta-ethylenic unsaturation, such as the  $C_4$ - $C_{12}$  alpha olefins, for example isobutylene, hexene, nonene, dodecene, etc.; styrenes, for example styrene, alpha-methyl styrene, p-methyl styrene, p-sec. butyl styrene, etc.; and vinyl monomers, for example vinyl acetate, vinyl chloride, vinyl ketones such as methyl and ethyl vinyl ketone, etc. Comonomers containing functional groups which may cause crosslinking, gelation or other interfering reactions should be avoided, although minor amounts of such comonomers (up to about 10% by weight of the comonomer system) often can be tolerated.

Specific useful copolymerizable comonomers include the following:

(A) Esters of saturated acids and unsaturated alcohols wherein the saturated acids may be monobasic or polybasic acids containing up to about 40 carbon atoms such as the following: acetic, propionic, butyric, valeric, caproic, stearic, oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, phthalic, isophthalic, terephthalic, hemimellitic, trimellitic, trimesic and the like, including mixtures. The unsaturated alcohols may be monohydroxy or polyhydroxy alcohols and may contain up to about 40 carbon atoms, such as the following: allyl, methallyl, crotyl, 1-chloroallyl, 2-chloroallyl, cinnamyl, vinyl, methyl vinyl, 1-phenallyl, butenyl, propargyl, 1-cyclohexene-3-ol, oleyl, and the like, including mixtures.

(B) Esters of unsaturated monocarboxylic acids containing up to about 12 carbon atoms such as

acrylic, methacrylic and crotonic acid, and an esterifying agent containing up to about 50 carbon atoms, selected from saturated alcohols and alcohol epoxides. The saturated alcohols may preferably contain up to about 40 carbon atoms and include monohydroxy compounds such as: methanol, ethanol, propanol, butanol, 2-ethylhexanol, octanol, dodecanol, cyclohexanol, cyclopentanol, neopentyl alcohol, and benzyl alcohol; and alcohol ethers such as the monomethyl or monobutyl ethers of ethylene or propylene glycol, and the like, including mixtures. The alcohol epoxides include fatty alcohol epoxides, glycidol, and various derivatives of alkylene oxides, epichlorohydrin, and the like, including mixtures.

The components of the graft copolymerizable system are used in a ratio of unsaturated acid monomer component to comonomer component of about 1:4 to 4:1, preferably about 1.2 to 2:1 by weight.

#### GRAFTING OF THE ETHYLENE COPOLYMER

The grafting of the ethylene copolymer with the ethylenically unsaturated carboxylic acid material may be by any suitable method, such as thermally by the "ene" reaction, using copolymers containing unsaturation, such as ethylene-propylene-diene polymers either chlorinated or unchlorinated, extruder or masticator grafting, or more preferably it is by free-radical induced grafting in solvent, preferably in a mineral lubricating oil as solvent.

The free-radical induced grafting of ethylenically unsaturated carboxylic acid materials in solvents, such as benzene, is known in the art and disclosed, inter alia, in U.S. Patent No. 2,236,917, incorporated herein by reference. The free-radical grafting is preferably carried out using free radical initiators such as peroxides and hydroperoxides, and nitrile compounds, preferably those which have a boiling point greater than about 100°C and which decompose thermally within the grafting temperature range to provide said free radicals. Representative of these free-radical initiators are azobutyro-nitrile, 2,5-dimethyl-hex-3-yne-2, 5-bis-tertiary-butyl peroxide (sold as Luperso 130) or its hexane analogue, di-tertiary butyl peroxide and dicumyl peroxide. The initiator is generally used at a level of between about 0.005% and about 1%, based on the total weight of the polymer solution, and temperatures of about 150 to 220°C.

The ethylenically unsaturated carboxylic acid material, preferably maleic anhydride, will be generally used in an amount ranging from about 0.01% to about 10%, preferably 0.1 to 2.0%, based on weight of the initial total solution. The aforesaid carboxylic acid material and free radical initiator are generally used in a weight percent ratio of ethylenically unsaturated carboxylic acid material to free radical initiator of about 1.0:1 to 30:1, preferably 3.0:1 to 6:1.

The initiator grafting is preferably carried out in an inert atmosphere, such as that obtained by nitrogen blanketing. While the grafting can be carried out in the presence of air, the yield of the desired graft polymer is generally thereby decreased as compared to grafting under an inert atmosphere substantially free of oxygen. The grafting time will usually range from about 0.1 to 12 hours, preferably from about 0.5 to 6 hours, more preferably 0.5 to 3 hours. The graft reaction will be usually carried out to at least approximately 4 times, preferably at least about 6 times the half-life of the free-radical initiator at the reaction temperature employed, e.g. with 2,5-dimethyl hex-3-yne-2, 5-bis(t-butyl peroxide) 2 hours at 160°C. and one hour at 170°C., etc.

In the grafting process, usually the copolymer solution is first heated to grafting temperature and thereafter said unsaturated carboxylic acid material and initiator are added with agitation, although they could have been added prior to heating. When the reaction is complete, the excess acid material can be eliminated by an inert gas purge, e.g. nitrogen sparging. Preferably the carboxylic acid material that is added is kept below its solubility limit in the polymer solution, e.g. below about 1 wt. %, preferably below 0.4 wt. % or less, of free maleic anhydride based on the total weight of polymer-solvent solution, e.g. ethylene copolymer mineral lubricating oil solution. Continuous or periodic addition of the carboxylic acid material along with an appropriate portion of initiator, during the course of the reaction, can be utilized to maintain the carboxylic acid below its solubility limits, while still obtaining the desired degree of total grafting.

In the grafting step the maleic anhydride or other carboxylic acid material used may be grafted onto both the polymer and the solvent for the reaction. Many solvents such as dichlorobenzene are relatively inert and may be only slightly grafted, while mineral oil will tend to be more grafted. The exact split of graft between the substrates present depends upon the polymer and its reactivity, the  $r$  activity and type of solvent, the concentration of the polymer in the solvent, and also upon the maintenance of the carboxylic acid material in solution during the course of the reaction and minimizing the presence of dispersed, but undissolved acid, e.g. the maleic anhydride. The undissolved acid material appears to have an increased

tendency to react to form oil insoluble materials as opposed to dissolved acid material. The split between grafted solvent and grafted polymer may be measured empirically from the infrared analyses of the product dialyzed into solvent and polymer fractions.

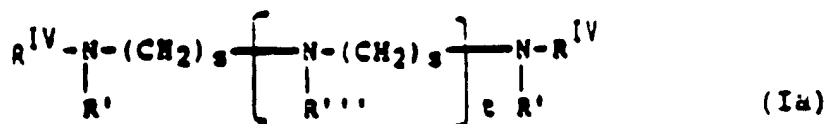
The grafting is preferably carried out in a mineral lubricating oil which need not be removed after the grafting step but can be used as the solvent in the subsequent reaction of the graft polymer with the amine material and as a solvent for the end product to form the lubricating additive concentrate. The oil having attached, grafted carboxyl groups, when reacted with the amine material will also be converted to the corresponding derivatives.

The solution grafting step when carried out in the presence of a high temperature decomposable peroxide can be accomplished without substantial degradation of the chain length (molecular weight) of the ethylene containing polymer.

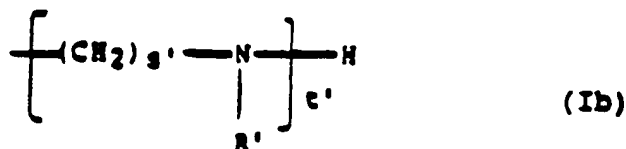
### THE POLYAMINES

The amine component which may be reacted with the grafted ethylene copolymer will generally have two or more reactive amine groups selected from primary and secondary amine groups, preferably primary amine groups.

Preferred amines are aliphatic saturated amines, including those of the general formulae:



wherein  $R^{IV}$ ,  $R'$ ,  $R''$  and  $R'''$  are independently selected from the group consisting of hydrogen;  $C_1$  to  $C_{25}$  straight or branched chain alkyl radicals;  $C_1$  to  $C_{12}$  alkoxy  $C_2$  to  $C_6$  alkylene radicals;  $C_2$  to  $C_{12}$  hydroxy amino alkylene radicals; and  $C_1$  to  $C_{12}$  alkylamino  $C_2$  to  $C_6$  alkylene radicals; and wherein  $R''$  and  $R'''$  can additionally comprise a moiety of the formula

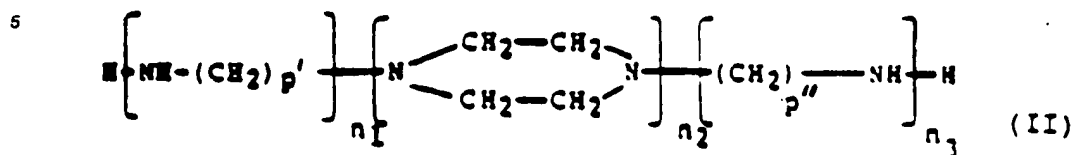


wherein  $R'$  is as defined above, and wherein each  $s$  and  $s'$  can be the same or a different number of from 2 to 6, preferably 2 to 4; and  $t$  and  $t'$  can be the same or different and are each numbers of typically from 0 to 10, preferably about 2 to 7, most preferably about 3 to 7, with the proviso that  $t + t'$  is not greater than 10. To assure a facile reaction it is preferred that  $R^{IV}$ ,  $R'$ ,  $R''$ ,  $R'''$ ,  $(s)$ ,  $(s')$ ,  $(t)$  and  $(t')$  be selected in a manner sufficient to provide the compounds of formula Ia with typically at least two primary amino groups. This can be achieved by selecting at least one of said  $R^{IV}$ ,  $R'$ , or  $R''$  groups to be hydrogen or by letting  $(t)$  in formula Ia be at least one when  $R''$  is H or when the (Ib) moiety possesses a primary amino group.

Non-limiting examples of suitable amine compounds include: 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; polypropylene amines such as 1,2-propylene diamine; di-(1,2-propylene) triamine; di-(1,3-propylene) triamine; N,N-dimethyl-1,3-diaminopropane; N,N-di-(2-aminoethyl) ethylene diamine; N,N-di(2-hydroxyethyl)-1,3-propylene diamine; N-dodecyl-1,3-propane diamine; and mixtures

thereof.

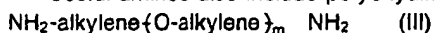
Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminoethyl) cyclohexane, and N-aminoalkyl piperazines of the general formula:



wherein  $p_1$  and  $p_2$  are the same or different and are each integers of from 1 to 4, and  $n_1$ ,  $n_2$  and  $n_3$  are the same or different and are each integers of from 1 to 3.

Commercial mixtures of amine compounds may advantageously be used. For example, one process for preparing alkylene amines involves the reaction of an alkylene dihalide (such as ethylene dichloride or propylene dichloride) with ammonia, which results in a complex mixture of alkylene amines wherein pairs of nitrogens are joined by alkylene groups, forming such compounds as diethylene triamine, triethylenetetramine, tetraethylene pentamine and corresponding piperazines. Low cost poly(ethyleneamine) compounds averaging about 5 to 7 nitrogen atoms per molecule are available commercially under trade names such as "Polyamine H", "Polyamine 400", "Dow Polyamine E-100", etc.

Useful amines also include polyoxyalkylene polyamines such as those of the formulae:

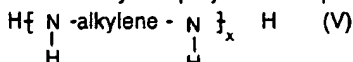


where  $m$  has a value of about 3 to 70 and preferably 10 to 35; and



where  $n$  has a value of about 1 to 40, with the provision that the sum of all the  $n$ 's is from about 3 to about 70, and preferably from about 6 to about 35, and  $\text{R}^V$  is a substituted saturated hydrocarbon radical of up to 10 carbon atoms, wherein the number of substituents on the  $\text{R}^V$  group is from 3 to 6, and "a" is a number from 3 to 6 which represents the number of substituents on  $\text{R}^V$ . The alkylene groups in either formula (III) or (IV) may be straight or branched chains containing about 2 to 7, and preferably about 2 to 4 carbon atoms.

Particularly preferred polyamine compounds are the polyoxyalkylene polyamines of formulae III and IV, and the alkylene polyamines represented by the formula



wherein  $x$  is an integer of about 1 to 10, preferably about 2 to 7, and the alkylene radical is a straight or branched chain alkylene radical having 2 to 7, preferably about 2 to 4 carbon atoms.

Examples of the alkylene polyamines of formula (V) include methylene amines, ethylene amines, butylene amines, propylene amines, pentylene amines, hexylene amines, heptylene amines, octylene amines, other polymethylene amines, the cyclic and higher homologs of these amines such as the piperazines, the amino-alkyl-substituted piperazines, etc. These amines include, for example, ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, di-(heptamethylene)triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di-(trimethylene)triamine, 2-heptyl-3-(2-aminopropyl)-imidazoline, 4-methylimidazoline, 1,3-bis-(2-aminopropyl)-imidazoline, pyrimidine, 1-(2-aminopropyl)piperazine, 1,4-bis(2-aminoethyl)piperazine, N,N-dimethylaminopropyl amine, N,N-dioctylethyl amine, N-octyl-N'-methyleneethylene diamine, 2-methyl-1-(2-aminobutyl)piperazine, etc. Other higher homologs which may be used can be obtained by condensing two or more of the above-mentioned alkylene amines in a known manner.

The ethylene amines which are particularly useful are described, for example, in the Encyclopedia of Chemical Technology under the heading of "Ethylene Amines" (Kirk and Othmer), Volume 5, pgs. 898-905; Interscience Publishers, New York (1950), incorporated herein by reference. These compounds are prepared by the reaction of an alkylene chloride with ammonia. This results in the production of a complex mixture of alkylene amines, including cyclic condensation products such as piperazines. While mixtures of these amines may be used for purposes of this invention, it is obvious that pure alkylene amines may be used with complete satisfaction.

The polyoxyalkylene polyamines of formulae III and IV, preferably polyoxyalkylene diamines and polyoxyalkylene triamines, may have average molecular weights ranging from about 200 to about 4000 and preferably from about 400 to about 2000. The preferred polyoxyalkylene polyamines include the polyoxyethylene and the polyoxypropylene diamines and the polyoxypropylene triamines having average molecular weights ranging from about 200 to 2000. The polyoxyalkylene polyamines are commercially available



and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403", etc.

## POLYOL

In another aspect of the invention the grafted ethylene copolymer is reacted with a polyol instead of with a polyamine.

Suitable polyol compounds which can be used include aliphatic polyhydric alcohols containing up to about 100 carbon atoms and about 2 to about 10 hydroxyl groups. These alcohols can be quite diverse in structure and chemical composition, for example, they can be substituted or unsubstituted, hindered or unhindered, branched chain or straight chain, etc. as desired. Typical alcohols are alkylene glycols such as ethylene glycol, propylene glycol, trimethylene glycol, butylene glycol, and polyglycols such as diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and other alkylene glycols and polyalkylene glycols in which the alkylene radical contains from two to about eight carbon atoms. Other useful polyhydric alcohols include glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, tripentaerythritol, 9,10-dihydroxystearic acid, the ethyl ester of 9,10-dihydroxystearic acid, 3-chloro-1,2-propanediol, 1,2-butanediol, 1,4-butanediol, 2,3-hexanediol, pinacol, tetrahydroxy pentane, erythritol, arabitol, sorbitol, mannitol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,4-(2-hydroxyethyl)-cyclohexane, 1,4-dihydroxy-2-nitrobutane, 1,4-di-(2-hydroxyethyl)-benzene, and the carbohydrates such as glucose, mannose, glyceraldehyde, galactose, and the like.

Included within the group of aliphatic alcohols are those alkane polyols which contain ether groups such as polyethylene oxide repeating units, as well as those polyhydric alcohols containing at least three hydroxyl groups, at least one of which has been esterified with a mono-carboxylic acid having from eight to about 30 carbon atoms such as octanoic acid, oleic acid, stearic acid, linoleic acid, dodecanoic acid, or tall oil acid. Examples of such partially esterified polyhydric alcohols are the mono-oleate of sorbitol, the mono-oleate of glycerol, the monostearate of glycerol, the di-stearate of sorbitol, and the di-dodecanoate of erythritol.

A preferred class of aliphatic alcohols are those containing up to 20 carbon atoms, and especially those containing three to 15 carbon atoms. This class of alcohols includes glycerol, erythritol, pentaerythritol, dipentaerythritol, tripentaerythritol, gluconic acid, glyceraldehyde, glucose, arabinose, 1,7-heptanediol, 2,4-heptanediol, 1,2,3-hexanetriol, 1,2,4-hexanetriol, 1,2,5-hexanetriol, 2,3,4-hexanetriol, 1,2,3-butanetriol, 1,2,4-butanetriol, 2,2,6,6-tetrakis(hydroxymethyl)-cyclohexanol, 1,10-decanediol, and the like.

An especially preferred class of polyhydric alcohols are the polyhydric alkanols containing three to 15, especially three to six carbon atoms and having at least three hydroxyl groups. Such alcohols are exemplified in the above specifically identified alcohols and are represented by glycerol, erythritol, pentaerythritol, mannitol, sorbitol, 1,2,4-hexanetriol, and tetrahydroxy pentane and the like.

## THE POLY-N-BUTENE SUBSTITUTED CARBOXYLIC ACID MATERIAL

The poly-n-butene substituted dicarboxylic acid material which is used to make the multifunctional viscosity index improver of the instant invention includes the reaction product of poly-n-butene with (i) monounsaturated  $C_4$  to  $C_{10}$  dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, i.e., located on adjacent carbon atoms, and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; or with (ii) derivatives of (i) such as anhydrides or  $C_1$  to  $C_5$  alcohol derived mono- or diesters of (i). Upon reaction with the n-butene polymer, the monounsaturations of the dicarboxylic acid, anhydride, or ester becomes saturated. Thus, for example, maleic anhydride becomes a poly-n-butene substituted succinic anhydride.

Typically, from about 0.7 to about 4.0, (e.g., 0.7 to 2.6) preferably from about 1.0 to about 2.0, and most preferably from about 1.1 to about 1.7 moles of said unsaturated  $C_4$  to  $C_{10}$  dicarboxylic acid, anhydride or ester are charged to the reactor per mole of polynormalbutene charged.

Normally, not all of the poly-n-butene reacts with the unsaturated acid or derivative and the poly-n-butene substituted dicarboxylic acid material will contain unreacted poly-n-butene. The unreacted poly-n-butene is typically not removed from the reaction mixture (because such removal is difficult and would be commercially infeasible) and the product mixture, stripped of any unreacted monounsaturated  $C_4$  to  $C_{10}$

dicarboxylic acid, anhydride, or ester is employed for further reaction with the amine as described hereinafter.

Characterization of the average number of moles of dicarboxylic acid, anhydride, or ester, which have reacted per mole of poly-n-butene charged to the reaction (whether it has undergone reaction or not) is defined herein as functionality. Said functionality is based upon (i) determination of the saponification number of the resulting product mixture using potassium hydroxide; and (ii) the number average molecular weight of the poly-n-butene charged, using techniques well known in the art. Functionality is defined solely with reference to the resulting product mixture. Although the amount of said reacted poly-n-butene contained in the resulting product mixture can be subsequently modified, i.e. increased or decreased by techniques known in the art, such modifications do not alter functionality as defined above. The term poly-n-butene substituted dicarboxylic acid material is intended to refer to the product mixture whether it has undergone such modification or not.

Accordingly, the functionality of the poly-n-butene substituted dicarboxylic acid material will be typically at least about 0.5, preferably at least about 0.8, and most preferably at least about 0.9, and will vary typically from about 0.5 to about 2.8 (e.g., 0.6 to 2), preferably from about 0.8 to about 1.4, and most preferably from about 0.9 to about 1.3.

To form the poly-n-butene substituted dicarboxylic acid material the ethylenically unsaturated dicarboxylic acid material, i.e., acid, anhydride or ester, is reacted with a n-butene polymer. The n-butene polymers will usually have number average molecular weights ( $\overline{M}_n$ ) within the range of about 300 to about 3,000, preferably between about 400 and 2,000. The n-butene polymers are derived from n-butene monomers. Generally, these n-butene polymers are derived from mixtures of n-butene-1 and n-butene-2 (both cis and trans) monomers. Generally, such monomer mixtures contain from about 40-90 wt.% n-butene-1 and from about 10-50 wt.% n-butene-2 monomers, preferably from about 50-90 wt.% n-butene-1 and from about 10-50 wt.% n-butene-2 monomers. These monomer mixtures may also contain minor amounts, i.e., below about 5 wt% of isobutene monomers. The isobutene monomers is, however, present merely as an impurity or byproduct resulting from the processes used to produce the n-butene-1 and n-butene-2 monomers. It is desirable to minimize the amount of isobutene monomer present in the monomer mixture.

Therefore, when the term poly-n-butene or n-butene polymer is used in the specification and claims it refers to a polymer derived from a mixture containing about 95-100 wt.% n-butene-1 and n-butene-2 monomers as described above, and from 0 to about 5 wt. % of isobutene monomer.

Processes for reacting the n-butene polymer with the  $C_4$ - $C_{10}$  unsaturated dicarboxylic acid, anhydride or ester are known in the art. For example, the n-butene polymer and the dicarboxylic acid material may be simply heated together as disclosed in U.S. Pat. Nos. 3,361,673 and 3,401,118 to cause a thermal "ene" reaction to take place. Alternatively, the n-butene polymer can be first halogenated, for example, chlorinated or brominated to about 1 to 8, preferably 3 to 7 wt. % chlorine or bromine, based on the weight of polymer, by passing the chlorine or bromine through the polynormalbutene at a temperature of 60 to 160 °C, e.g., 110. to 130 °C, for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer may then be reacted with sufficient unsaturated acid or anhydride at 100 to 250 °C, usually about 180 to 235 °C, for about 0.5 to 10 hours, e.g. 3 to 8 hours. Processes of this general type are taught, inter alia, in U.S. Patents 3,087,438; 3,172,892; 3,272,746; and EP-A-0264247.

Alternatively, the poly-n-butene and the unsaturated acid material are mixed and heated while adding chlorine to the hot material. Processes of this type are disclosed in U.S. Patents 3,215,707; 3,231,587; 3,912,764; 4,110,349; 4,234,435; and in U.K. 1,440,219, all of which are incorporated herein by reference.

By the use of halogen, about 65 to 95 wt. % of the poly-n-butene, will normally react with the dicarboxylic acid material. Upon carrying out a thermal reaction without the use of halogen or a catalyst, then usually only about 50 to 85 wt. % of the poly-n-butene will react. Chlorination helps increase the reactivity.

The preferred poly-n-butene substituted dicarboxylic acid material is poly-n-butene succinic anhydride or acid, preferably the anhydride.

#### REACTION OF GRAFTED ETHYLENE COPOLYMERS AND POLY-N-BUTENE SUBSTITUTED DICARBOXYLIC ACID MATERIALS WITH POLYAMINE OR POLYOL

The grafted ethylene copolymer, preferably in solution generally equal to about 5 to 30 wt. %, preferably 10 to 20 wt. % polymer, can be readily reacted with a mixture of polyamine or polyol and poly-n-butene substituted dicarboxylic acid material by heating said mixture at a temperature of from about 100 °C

to 250° C, preferably from 150° to 200° C, for from 0.1 to 10 hours, usually about 0.5 to about 3 hours. The heating is preferably carried out to favor, in the case of polyamines, formation of imides rather than amides and salts. Thus, imide formation will give a lower viscosity of the reaction mixture than amide formation and particularly lower than salt formation. This lower viscosity permits the utilization of a higher concentration of grafted ethylene copolymer in the reaction mixture. Removal of water, e.g., by N<sub>2</sub> stripping, during slow addition of the amine with stirring assures completion of the imidation reaction. Reaction ratios can vary considerably, depending upon the reactants, amounts of excess, type of bonds formed, etc. The amount of polyamine or polyol used is an amount effective to enhance or improve the dispersant properties of the compounds of the instant invention. Generally, in the case of the polyamine, the amount of polyamine used is an amount which is effective to provide from about 0.5 to about 1.5 equivalents, preferably from about 0.8 to about 1.2 equivalents, and more preferably from about 0.9 to about 1.0 equivalents of primary amine per equivalent of acid of the grafted dicarboxylic acid moiety e.g., succinic anhydride.

The amount of poly-n-butene substituted dicarboxylic acid material utilized is an amount which is effective to prevent cross-linking or excessive chain-extension of the grafted ethylene copolymer during amination/imidation thereof. Generally, this amount is from about 1 to about 4, preferably about 1.5 to 3, most preferably about 2, mole equivalents of said poly-n-butene substituted dicarboxylic acid material per mole of said dicarboxylic acid moiety content in the grafted ethylene copolymer. Alternatively, if pre-reacted amine and poly-n-butene substituted dicarboxylic acid material adduct, as described hereinafter, is used, sufficient adduct is used to provide about 1 to 2 reactive, e.g., primary, amine groups per dicarboxylic acid moiety in the grafted ethylene copolymer, depending upon whether primarily imides or amides are formed. Usually, 1 to 2 moles of said adduct are used per molar amount of said dicarboxylic acid moieties in the grafted copolymer. For example, with an ethylene-propylene copolymer of about 40,000  $\overline{M}_n$ , a thickening efficiency of about 2.1, and averaging 4 succinic anhydride groups per molecule, and making imides, about 4 moles of amine with two primary amine groups and about 4 moles of poly-n-butene substituted succinic anhydride would preferably be used per mole of grafted ethylene copolymer.

Alternatively, the polyamine and the poly-n-butene substituted dicarboxylic acid material may be pre-reacted to form an amine-acid adduct, and this adduct may then be reacted with the grafted ethylene copolymer. In the amine-acid adduct the acid moiety of the poly-n-butene substituted dicarboxylic acid material is generally attached to the polyamine moiety through salt, imide, amide, amidine, or other linkages formed with one reactive, e.g., primary, amine group of said polyamine so that another reactive, e.g., primary, amine group of the polyamine is still available for reaction with the acid moieties of the grafted ethylene copolymer.

Usually, these adducts are made by condensing the poly-n-butene substituted dicarboxylic material, preferably a succinic acid or anhydride with a polyamine such as those described above under "The Amines".

The general formation of dicarboxylic acid polyamine adduct by reaction of polyamine with poly-n-butene succinic anhydride prepared from the reaction of a poly-n-butene or chlorinated polynormalbutene and maleic anhydride, etc. is known in the art, as seen in U.S. Pat. No. 3,272,746.

Reaction, in the case of a polyamine, preferably amination and/or imidation of the poly-n-butene substituted dicarboxylic acid material can be done as a solution reaction with said dicarboxylic acid material, preferably poly-n-butene succinic anhydride, dissolved in a solvent such as mineral oil, to which the other reactant is added. The formation of the adducts in high yield can be effected by adding from about 0.5 to 3.3 preferably about 0.7 to 1.3, most preferably about 1 molar proportion of the alkylene polyamine per molar proportion of poly-n-butene succinic anhydride to said solution and heating the mixture at 140° C to 175° C or higher until the appropriate amount of water of reaction is evolved. Typically the mineral oil solvent is adjusted so that it constitutes 50% by weight of the final acyl nitrogen compound solution.

Another, and generally preferred, method of making the multi-functional viscosity index improvers of the instant invention is a sequential reaction process comprising (i) forming the grafted ethylene copolymer, (ii) adding to said grafted ethylene copolymer the poly-n-butene substituted dicarboxylic acid material so as to form a mixture of said grafted ethylene copolymer and said poly-n-butene substituted dicarboxylic acid material, and (iii) reacting this mixture with the polyamine or polyol.

A minor amount, e.g. 0.001 up to 50 wt. %, preferably 0.005 to 25 wt. %, based on the weight of the total composition, of the oil-soluble functionalized graft ethylene copolymers produced in accordance with this invention can be incorporated into a major amount of an oleaginous material, such as lubricating oil or hydrocarbon fuel, depending upon whether one is forming finished products or additives concentrates. When used in lubricating oil compositions, e.g. automotive or diesel crankcase lubricating oil, the nitrogen-containing or ester-containing grafted polymer concentrations are usually within the range of about 0.01 to

10 wt. %, e.g. 0.1 to 6.0 wt. %, preferably 0.25 to 3.0 wt. %, of the total composition. The lubricating oils to which the products of this invention can be added include not only hydrocarbon oil derived from petroleum, but also include synthetic lubricating oils such as esters of dibasic acids; complex esters made by esterification of monobasic acids, polyglycols, dibasic acids and alcohols; polyolefin oils, etc.

6 The multi-functional viscosity index improvers of the instant invention may be utilized in a concentrate form, e.g., from about 5 wt. % up to about 50 wt. %, preferably 7 to 25 wt. %, in oil, e.g., mineral lubricating oil, for ease of handling, and may be prepared in this form by carrying out the reaction of the invention in oil as previously discussed.

The compositions produced in accordance with the present invention have been found to be particularly useful as fuel and lubricating oil additives.

When the compositions of this invention are used in normally liquid petroleum fuels, such as middle distillates boiling from about 65° to 430° F. including kerosene, diesel fuels, home heating fuel oil, jet fuels, etc., a concentration of the additive in the fuel in the range of typically from 0.001 wt. % to 0.5 wt. %, preferably 0.005 wt. % to 0.2 wt. %, based on the total weight of the composition, will usually be employed.

15 These additives can contribute fuel stability as well as dispersant activity and/or varnish control behavior to the fuel.

The compounds of this invention find their primary utility, however, in lubricating oil compositions, which employ a base oil in which the additives are dissolved or dispersed. Such base oils may be natural or synthetic.

20 Thus, base oils suitable for use in preparing the lubricating compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Advantageous results are also achieved by employing the additives of the present invention in base oils conventionally employed in and/or adapted for use as power transmitting fluids such as automatic transmission fluids, tractor fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil compositions can also benefit from the incorporation therein of the additives of the present invention.

Thus, the additives of the present invention may be suitably incorporated into synthetic base oils such as alkyl esters of dicarboxylic acids, polyglycols and alcohols; polyalpha-olefins, polybutenes, alkyl benzenes, organic esters of phosphoric acids, polysilicone oils, etc. selected type of lubricating oil composition can be included as desired.

The additives of this invention are oil-soluble, dissolvable in oil with the aid of a suitable solvent, or are stably dispersible materials. Oil-soluble, dissolvable, or stably dispersible as that terminology is used herein does not necessarily indicate that the materials are soluble, dissolvable, miscible, or capable of being suspended in oil in all proportions. It does mean, however, that the additives, for instance, are soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular polymer adduct hereof, if desired.

40 Accordingly, while any effective amount of these additives can be incorporated into the fully formulated lubricating oil composition, it is contemplated that such effective amount be sufficient to provide said lube oil composition with an amount of the additive of typically from 0.01 to about 10, e.g., 0.1 to 6.0, and preferably from 0.25 to 3.0 wt. %, based on the weight of said composition.

The additives of the present invention can be incorporated into the lubricating oil in any convenient way. Thus, they can be added directly to the oil by dispersing, or dissolving the same in the oil at the desired level of concentration, typically with the aid of a suitable solvent such as toluene, cyclohexane, or tetrahydrofuran. Such blending can occur at room temperature or elevated.

Natural base oils include mineral lubricating oils which may vary widely as to their crude source, e.g., whether paraffinic, naphthenic, mixed, paraffinic-naphthenic, and the like; as well as to their formation, e.g., distillation range, straight run or cracked, hydrofined, solvent extracted and the like.

50 More specifically, the natural lubricating oil base stocks which can be used in the compositions of this invention may be straight mineral lubricating oil or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crudes, or, if desired, various blends oils may be employed as well as residuals, particularly those from which asphaltic constituents have been removed. The oils may be refined by conventional methods using acid, alkali, and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichlorodimethyl ether, nitrobenzene, crotonaldehyde, etc.

The lubricating oil base stock conveniently has a viscosity of typically about 2.5 to about 12, and

preferably about 2.5 to about 9 cSt. at 100 °C.

Thus, the additives of the present invention can be employed in a lubricating oil composition which comprises lubricating oil, typically in a major amount, and the additive, typically in a minor amount, which is effective to impart enhanced dispersancy relative to the absence of the additive. Additional conventional additives selected to meet the particular requirements of a temperatures. In this form the additive per se is thus being utilized as a 100% active ingredient form which can be added to the oil or fuel formulation by the purchaser. Alternatively, these additives may be blended with suitable oil-soluble solvent and base oil to form concentrate, which may then be blended with a lubricating oil base stock to obtain the final formulation. Concentrates will typically contain from about 2 to 80 wt. %, by weight of the additive, and preferably from about 5 to 40% by weight of the additive.

The lubricating oil base stock for the additive of the present invention typically is adapted to perform selected function by the incorporation of additives therein to form lubricating oil compositions (i.e., formulations).

Representative additives typically present in such formulations include other viscosity modifiers, corrosion inhibitors, oxidation inhibitors, friction modifiers, other dispersants, anti-foaming agents, anti-wear agents, pour point depressants, detergents, rust inhibitors and the like.

Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain shear stable at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. These viscosity modifiers are generally high molecular weight hydrocarbon polymers including polyesters. The viscosity modifiers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties.

These oil soluble viscosity modifying polymers will generally have weight average molecular weights of from about 10,000 to 1,000,000, preferably 20,000 to 500,000, as determined by gel permeation chromatography or light scattering methods.

Representative examples of suitable viscosity modifiers are any of the types known to the art including polyisobutylene, copolymers of ethylene and propylene, polymethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and vinyl compound, interpolymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C<sub>2</sub> to C<sub>6</sub> olefin polymer such as polyisobutylene, with from 5 to 30 wt. % of a sulfide of phosphorus for 1/2 to 15 hours, at temperature in the range of about 66 to about 316 °C. Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner taught in U.S. Patent No. 1,969,324.

Oxidation inhibitors, or antioxidants, reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkylphenolthioesters having preferably C<sub>5</sub> to C<sub>12</sub> alkyl side chains, e.g., calcium nonylphenol sulfide, barium toctylphenyl sulfide, dioctylphenylamine, phenylalphanaphthylamine, phospho-sulfurized or sulfurized hydrocarbons, etc.

Other oxidation inhibitors or antioxidants useful in this invention comprise oil-soluble copper compounds. The copper may be blended into the oil as any suitable oil soluble copper compound. By oil soluble it is meant that the compound is oil soluble under normal blending conditions in the oil or additive package. The copper compound may be in the cuprous or cupric form. The copper may be in the form of the copper dihydrocarbyl thio- or dithio-phosphates. Alternatively, the copper may be added as the copper salt of a synthetic or natural carboxylic acid. Examples of same thus include C<sub>10</sub> to C<sub>18</sub> fatty acids, such as stearic or palmitic acid, but unsaturated acids such as oleic or branched carboxylic acids such as naphthenic acids of molecular weights of from about 200 to 500, or synthetic carboxylic acids, are preferred, because of the improved handling and solubility properties of the resulting copper carboxylates. Also useful are oil-soluble copper dithiocarbamates of the general formula (R<sup>20</sup>R<sup>21</sup>,NCSS)<sub>2</sub>Cu (where z is 1 or 2, and R<sup>20</sup> and R<sup>21</sup>, are the same or different hydrocarbyl radicals containing from 1 to 18, and preferably 2 to 12, carbon atoms, and including radicals such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R<sup>20</sup> and R<sup>21</sup>, groups are alkyl groups of from 2 to 8 carbon atoms. Thus, the

radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-heptyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl, etc. In order to obtain oil solubility, the total number of carbon atoms (i.e.,  $R^{20}$  and  $R^{21}$ ), will generally be about 5 or greater. Copper sulphonates, phenates, and acetylacetonates may also be used.

5 Exemplary of useful copper compounds are copper  $Cu^I$  and/or  $Cu^{II}$  salts of alkenyl succinic acids or anhydrides. The salts themselves may be basic, neutral or acidic. They may be formed by reacting (a) polyalkylene succinimides (having polymer groups of  $\overline{M}_n$  of 700 to 5,000) derived from polyalkylene-polyamines, which have at least one free carboxylic acid group, with (b) a reactive metal compound. Suitable reactive metal compounds include those such as cupric or cuprous hydroxides, oxides, acetates, 10 borates, and carbonates or basic copper carbonate.

Examples of these metal salts are Cu salts of polyisobutenyl succinic anhydride, and Cu salts of polyisobutenyl succinic acid. Preferably, the selected metal employed is its divalent form, e.g.,  $Cu^{+2}$ . The preferred substrates are polyalkenyl succinic acids in which the alkenyl group has a molecular weight greater than about 700. The alkenyl group desirably has a  $\overline{M}_n$  from about 900 to 1,400, and up to 2,500, 15 with a  $M_n$  of about 950 being most preferred. Especially preferred is polyisobutylene succinic anhydride or acid. These materials may desirably be dissolved in a solvent, such as a mineral oil, and heated in the presence of a water solution (or slurry) of the metal bearing material. Heating may take place between  $70^\circ C$  and about  $200^\circ C$ . Temperatures of  $100^\circ C$  to  $140^\circ C$  are entirely adequate. It may be necessary, depending upon the salt produced, not to allow the reaction to remain at a temperature above about  $140^\circ C$  20 for an extended period of time, e.g., longer than 5 hours, or decomposition of the salt may occur.

The copper antioxidants (e.g., Cu-polyisobutenyl succinic anhydride, Cu-oleate, or mixtures thereof) will be generally employed in an amount of from about 50 to 500 ppm by weight of the metal, in the final lubricating or fuel composition.

Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions such 25 as automatic transmission fluids.

Representative examples of suitable friction modifiers are found in U.S. Patent No. 3,933,659 which discloses fatty acid esters and amides; U.S. Patent No. 4,176,074 which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; U.S. Patent No. 4,105,571 which discloses glycerol esters of dimerized fatty acids; U.S. Patent No. 3,779,928 which discloses alkane phosphonic acid salts; 30 U.S. Patent No. 3,778,375 which discloses reaction products of a phosphonate with an oleamide; U.S. Patent No. 3,852,205 which discloses S-carboxyalkylene hydrocarbyl succinimide, S-carboxyalkylene hydrocarbyl succinamic acid and mixtures thereof; U.S. Patent No. 3,879,306 which discloses N-(hydroxyalkyl)alkenylsuccinamic acids or succinimides; U.S. Patent No. 3,932,290 which discloses reaction products of di- (lower alkyl) phosphites and epoxides; and U.S. Patent No. 4,028,258 which discloses the alkylene oxide adduct of phosphosulfurized N-(hydroxyalkyl) alkenyl succinimides. The disclosures of the 35 above references are herein incorporated by reference. The most preferred friction modifiers are succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides and thiobis-alkanols such as described in U.S. Patent 4,344,853.

Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid thus 40 preventing sludge flocculation and precipitation or deposition on metal parts. Suitable dispersants include high molecular weight alkyl succinimides, the reaction product of oil-soluble polyisobutylene succinic anhydride with ethylene amines such as tetraethylene pentamine and borated salts thereof.

Pour point depressants, otherwise known as lube oil flow improvers, lower the temperature at which the fluid will flow or can be poured. Such additives are well known. Typically of those additives which usefully 45 optimize the low temperature fluidity of the fluid are  $C_8$ - $C_{18}$  dialkylfumarate vinyl acetate copolymers, polymethacrylates, and wax naphthalene. Foam control can be provided by an antifoamant of the polysiloxane type, e.g., silicone oil and polydimethyl siloxane.

Anti-wear agents, as their name implies, reduce wear of metal parts. Representatives of conventional antiwear agents are zinc dialkyldithiophosphate and zinc diaryldithiophosphate.

50 Detergents and metal rust inhibitors include the metal salts of sulphonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates, naphthenates and other oil soluble mono- and dicarboxylic acids. Highly basic (viz. overbased) metal sales, such as highly basic alkaline earth metal sulfonates (especially Ca and Mg salts) are frequently used as detergents. Representative examples of such materials, and their methods of preparation, are found in EP-A-0208560.

55 Some of these numerous additives can provide a multiplicity of effects, e.g., a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

Compositions when containing these conventional additives are typically blended into the base oil in amounts which are effective to provide their normal attendant function. Representative effective amounts of

such additives are illustrated as follows:

	<u>Additive</u>	<u>Wt. % a.i.</u>	<u>Wt. % a.i.</u>
		(Broad)	(Preferred)
5	Viscosity Modifier	.01-12	.01-4
10	Corrosion Inhibitor	.01-5	.01-1.5
	Oxidation Inhibitor	.01-5	.01-1.5
15	Dispersant	.1-20	.1-8
20	Pour Point Depressant	.01-5	.01-1.5
	Anti-Foaming Agents	.001-3	.001-0.15
25	Anti-Wear Agents	.001-5	.001-1.5
30	<u>Additive</u>	<u>Wt. % a.i.</u>	<u>Wt. % a.i.</u>
		(Broad)	(Preferred)
35	Friction Modifiers	.01-5	.01-1.5
	Detergents/Rust Inhibitors	.01-10	.01-3
40	Mineral Oil Base	Balance	Balance

When other additives are employed it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the V.I.-dispersant (in concentrate amounts hereinabove described), together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to herein as an additive package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the V.I.-dispersant or multi-functional viscosity index improver additive and optional additional additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the products of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from about 2.5 to about 90%, and preferably from about 5 to about 75%, and most preferably from about 8 to about 50% by weight additives in the appropriate proportions with the remainder being base oil.

The final formulations may employ typically about 10 wt. % of the additive-package with the remainder being base oil.

All of said weight percents expressed herein are based on active ingredient (a.i.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the a.i. weight of each additive plus the weight of total oil or diluent.

This invention will be further understood by reference to the following examples, wherein all parts, unless otherwise indicated, are parts by weight and all molecular weights are number weight average molecular weights as noted, and which include preferred embodiments of the invention.

The following examples illustrate compositions falling outside the scope of the instant invention and are presented for comparative purposes only.

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#### COMPARATIVE EXAMPLE 1

Into a reactor vessel are placed 500 grams of an oil solution containing 20 weight percent of maleic anhydride grafted ethylene-propylene copolymer (EPSA) (having a graft level of 0.102 milliequivalent of succinic anhydride per gram of grafted material, an ethylene content of about 42-45%, a propylene content of about 55-58%, and a  $\overline{M}_n$  of about 30,000) in S100 NLP base oil. This solution is heated to 175 °C with stirring under a nitrogen atmosphere. To this solution are added 140.0 grams of an oil solution containing 50 weight % polyisobutenyl succinic anhydride (PIBSA); (having a polyisobutene  $\overline{M}_n$  of about 950, an SAP number of 112, and containing about 20% unreacted polyisobutene) in S100NLP base oil. The resultant reaction mixture is mixed with nitrogen stripping for one hour, and 5.7 grams of diethylenetriamine (DETA) are added to this reaction mixture over a period of 15 minutes. The reaction mixture is then stripped with nitrogen for 15 minutes. At the end of the strip, 3.25 grams of dodecylsuccinic anhydride are added to the system as end-capping agent.

The Shear Stability Index (SSI) and thickening efficiency (T.E.) of the EPSA-PIBSA-DETA polymer are determined and the results are set forth in Table I.

The Shear Stability Index is determined in accordance with ASTM D3945. The Shear Stability Index is an indication or measurement of the propensity of a polymer to degrade or breakdown to a lower molecular weight polymer upon exposure to shearing forces. The higher the SSI the more shear stable the polymer.

The thickening efficiency (T.E.) is defined as 2 divided by the number of grams of a polymer dissolved in a 100 gram blend of said polymer in a test oil, which is a solvent extracted neutral mineral lubricating oil having a viscosity of 6.04 CST at 100 °C, a viscosity index of 105 and an ASTM pour point of -25 °F, which will give a viscosity of 12.08 CST at 100 °C. The thickening efficiency is related to the number average molecular weight and is a more convenient, practical measurement.

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#### COMPARATIVE EXAMPLE 2

A lubricating oil composition formulated to 10W40 specifications with a standard detergent inhibitor package and containing 12.52 weight % of the reaction product of Comparative Example 1 is prepared by adding said reaction product to said oil. The CCS at -20 °C in centipoise and the Kinematic Viscosity at 100 °C in centistokes of this fully formulated lubricating oil composition is determined, and the results are set forth in Table I.

The following Examples illustrate compositions of the instant invention.

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#### EXAMPLE 3

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Into a reactor vessel are placed 314.9 grams of an oil solution containing 20 weight percent maleic anhydride grafted ethylene-propylene copolymer (EPSA) (having a graft level of 0.102 milliequivalent of succinic anhydride per gram of grafted material, an ethylene content of about 42-45%, a propylene content of about 55-58%, and a  $\overline{M}_n$  of about 30,000) in S100NLP base oil. This solution is heated to 190 °C with stirring under a nitrogen atmosphere. To this solution are added 97.22 grams of an oil solution containing 50 weight % poly-n-butene succinic anhydride (PNBSA) (having poly-n-butene  $\overline{M}_n$  of about 905, a SAP number of 90.9, and about 22.7% unreacted poly-n-butene, with said poly-n-butene being derived from a monomer mixture containing 65 wt% n-butene-1, 32 wt% n-butene-2, and 3 wt% isobutene) in S100NLP



base oil. The resultant reaction mixture is mixed with nitrogen stripping for 15 minutes and 3.62 grams of diethylenetriamine (DETA) are added to this reaction mixture over a period of 6 minutes. The reaction mixture is then stripped with nitrogen for 15 minutes. At the end of the strip, 2.05 grams of dodecylsuccinic anhydride are added to the system as capping agent.

5 The SSI and T.E. of the aminated EPSA polymer are determined and the results are set forth in Table I.

#### EXAMPLE 4

10 A lubricating oil composition formulated to 10W40 specifications with the standard detergent inhibitor package as used in Comparative Example 2 and containing 12.50 weight percent of the reaction product of Example 3 is prepared by adding said reaction product to said oil. The CCS at -20°C in centipoise and the Kinematic Viscosity at 100°C in centistokes of this fully formulated lubricating oil composition are  
15 determined, and the results are set forth in Table I.

TABLE I

20		COMPARATIVE EXAMPLE 2	EXAMPLE 4
	T.E.	1.65	1.69
	SSI	27.3%	28.5%
	K.V. in cSt at 100°C	15.07	14.71
25	CCS in centipoise at -20°C	3749	3255

As illustrated by the data in Table 1 the oil formulation containing the multifunctional viscosity index improver of the instant invention (Example 4) exhibits a much lower CCS, and, therefore, better low  
30 temperature viscometric properties, than the oil formulation containing a multifunctional viscosity index improver falling outside the scope of the instant invention (Comparative Example 2).

#### Claims

- 35 1. Oil soluble reaction product, useful as a multifunctional viscosity index improver for oleaginous compositions, comprising reaction product of:
  - (a) oil soluble ethylene copolymer comprising from 15 to 90 wt. % ethylene and from 10 to 85 wt. % of at least one C<sub>3</sub> to C<sub>28</sub> alpha-olefin, having a number average molecular weight of from 5,000 to 500,000,  
40 grafted with an ethylenically unsaturated carboxylic acid material having 1 to 2 carboxylic acid groups or anhydride group;
  - (b) organic polyamine having at least two reactive amine groups selected from primary and secondary amine groups, or polyol; and
  - (c) poly-n-butene substituted dicarboxylic acid material, said poly-n-butene having a number average  
45 molecular weight of from 300 to 3,000.
2. The reaction product according to claim 1 wherein said (c) is a poly-n-butene substituted succinic acid or anhydride.
3. The reaction product according to claim 1 or claim 2 wherein said poly-n-butene is derived from a monomer mixture comprised of n-butene-1 and n-butene-2.
- 50 4. The reaction product according to any of claims 1 to 3 wherein said ethylene copolymer of (a) is an ethylenepropylene copolymer.
5. The reaction product according to claim 4 wherein said (a) comprises a copolymer consisting essentially of 30 to 80 wt. % ethylene and 20 to 70 wt. % propylene, having a number-average molecular weight in the range of 10,000 to 200,000, grafted with maleic anhydride.
- 55 6. The reaction product according to any of claims 1 to 5 wherein the amount of (b) used is an amount effective to provide at least from 0.5 to 1.5 equivalents of primary amine per acid equivalent of the dicarboxylic acid material present in (a) and (c).
7. The reaction product according to any of claims 1 to 6 wherein (b) is polyamine, said polyamine

being an alkylene or oxyalkylene polyamine having at least two primary amine groups selected from the group consisting of alkylene polyamines having alkylene groups of 2 to 7 carbon atoms and 2 to 11 nitrogens, and polyoxyalkylene polyamines, wherein the alkylene groups contain 2 to 7 carbon atoms and the number of oxyalkylene groups is 3 to 70.

- 5 8. The reaction product according to claim 7 wherein said polyamine is diethylene triamine.
9. The reaction product according to any of claims 1 to 8 formed by simultaneously reacting (a), (b) and (c).
10. The reaction product according to any of claims 1 to 8 wherein (b) and (c) are first pre-reacted, followed by reaction with (a).
- 10 11. A lubricating oil composition exhibiting improved low temperature viscometric properties comprising (i) lubricating oil, and (ii) multifunctional viscosity index improver comprising the reaction product of any of claims 1 to 10.
12. The composition according to claim 11 which contains from 0.01 to 50 wt. % of said multifunctional viscosity index improver.
- 16 13. The composition according to claim 11 which is a lubricating oil concentrate.
14. The oleaginous composition according to any of claims 11 to 13 wherein (a) is comprised of an ethylene-propylene copolymer grafted with maleic anhydride, wherein (c) is comprised of poly-n-butene succinic anhydride, and wherein (b) is polyamine.
15. A process for preparing V.I.-dispersant exhibiting improved low temperature viscometric properties
- 20 comprising (i) grafting oil soluble ethylene copolymer having a number average molecular weight of from 5,000 to 500,000 and comprising 15 to 90 wt. % ethylene and 10 to 85 wt. % of at least one C<sub>3</sub> to C<sub>28</sub> olefin in an oil solution with at least one olefinically unsaturated dicarboxylic acid or anhydride using a free radical initiator at elevated temperatures; (ii) admixing with the grafted ethylene copolymer of (i) with poly-n-butene substituted dicarboxylic acid material to form a reaction mixture; and (iii) reacting said reaction
- 25 mixture with at least one polyamine containing at least two reactive amine groups selected from primary and secondary amine groups, or at least one polyol.
16. The process according to claim 15 wherein said ethylene copolymer is an ethylene-propylene copolymer having a number average molecular weight of from about 20,000 to 200,000, and comprises from about 30 to 80 wt. % ethylene and about 20 to 70 wt. % propylene.
- 30 17. The process according to claim 15 or claim 16 wherein said olefinically unsaturated dicarboxylic acid or anhydride is maleic acid or anhydride.
18. The process according to any of claims 15 to 17 wherein said poly-n-butene has a  $\overline{M}_n$  of from 300 to 3,000.

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DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)		
E	EP-A-0 352 070 (EXXON CHEMICAL PATENTS) * Claims 1-5,8,9,10-13,15-17; page 8, line 60 - page 9, line 2; page 14, example 3 *	1,2,4-18	C 10 M 143/02 C 08 F 255/02 C 10 M 145/10 C 10 M 149/06 C 10 M 159/12 //		
A	EP-A-0 146 162 (EXXON RESEARCH AND ENGINEERING CO.) * Claims 1-5; page 16, lines 1-37; page 19, lines 11-18; example * & US-A-4 517 104 (R. BLOCH) (Cat. D)	1,4-18	(C 10 M 143/02 C 10 M 143:00 ) (C 10 M 145/10 C 10 M 143:02 C 10 M 143:00 ) (C 10 M 149/06 C 10 M 143:02 C 10 M 143:00 ) (C 10 M 159/12 C 10 M 129:08 C 10 M 129:93 C 10 M 133:04 -/-		
P,A	EP-A-0 295 854 (EXXON CHEMICAL PATENTS) * Claims 1-3,6; page 15, example 4 *	1,4-8, 11-17			
A	US-A-4 632 769 (A. GUTIERREZ) * Claims 1-3,6-8,12,14; column 7, line 60 - column 8, line 37; column 10, example 1 *	1,4-17			
D,A	US-A-4 234 435 (N.A. MEINHARDT) * Claims 1,12,37; column 12, lines 49-55 *	1,2,7,8, 10-15, 18			
The present search report has been drawn up for all claims					
Place of search THE HAGUE		Date of completion of the search 02-02-1990	Examiner HILGENGA K.J.		
<table border="0"><tr><td><b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</td><td>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... &amp; : member of the same patent family, corresponding document</td></tr></table>				<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document	T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
			C 10 M 133:08 C 10 M 133:38 C 10 M 143:02 ) (C 08 F 255/02 C 08 F 222:06 ) (C 10 N 20/02 C 10 N 30:02 C 10 N 30:04 C 10 N 60:00 )
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-02-1990	Examiner HILGENA K.J.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			